

## X. APPENDIX I

### FEDERAL STANDARD FOR VINYL CHLORIDE (29 CFR 1910.1017)

#### § 1910.1017 Vinyl chloride.

(a) *Scope and application.* (1) This section includes requirements for the control of employee exposure to vinyl chloride (chloroethene), Chemical Abstracts Service Registry No. 75014.

(2) This section applies to the manufacture, reaction, packaging, repackaging, storage, handling or use of vinyl chloride or polyvinyl chloride, but does not apply to the handling or use of fabricated products made of polyvinyl chloride.

(3) This section applies to the transportation of vinyl chloride or polyvinyl chloride except to the extent that the Department of Transportation may regulate the hazards covered by this section.

(b) *Definitions.* (1) "Action level" means a concentration of vinyl chloride of 0.5 ppm averaged over an 8-hour work day.

(2) "Assistant Secretary" means the Assistant Secretary of Labor for Occupational Safety and Health, U.S. Department of Labor, or his designee.

(3) "Authorized person" means any person specifically authorized by the employer whose duties require him to enter a regulated area or any person entering such an area as a designated representative of employees for the purpose of exercising an opportunity to observe monitoring and measuring procedures.

(4) "Director" means the Director, National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare, or his designee.

(5) "Emergency" means any occurrence such as, but not limited to, equipment failure, or operation of a relief device which is likely to, or does, result in massive release of vinyl chloride.

(6) "Fabricated product" means a product made wholly or partly from polyvinyl chloride, and which does not require further processing at temperatures, and for times, sufficient to cause mass melting of the polyvinyl chloride resulting in the release of vinyl chloride.

(7) "Hazardous operation" means any operation, procedure, or activity where a release of either vinyl chloride liquid or gas might be expected as a consequence of the operation or because of an accident in the operation, which would result in an employee exposure in excess of the permissible exposure limit.

(8) "OSHA Area Director" means the Director for the Occupational Safety and Health Administration Area Office having jurisdiction over the geographic area in which the employer's establishment is located.

(9) "Polyvinyl chloride" means polyvinyl chloride homopolymer or copolymer before such is converted to a fabricated product.

(10) "Vinyl chloride" means vinyl chloride monomer.

(c) *Permissible exposure limit.* (1) No employee may be exposed to vinyl chloride at concentrations greater than 1 ppm averaged over any 8-hour period, and

(2) No employee may be exposed to vinyl chloride at concentrations greater than 5 ppm averaged over any period not exceeding 15 minutes.

(3) No employee may be exposed to vinyl chloride by direct contact with liquid vinyl chloride.

(d) *Monitoring.* (1) A program of initial monitoring and measurement shall be undertaken in each establishment to determine if there is any employee exposed, without regard to the use of respirators, in excess of the action level.

(2) Where a determination conducted under paragraph (d) (1) of this section shows any employee exposures, without regard to the use of respirators, in excess of the action level, a program for determining exposures for each such employee shall be established. Such a program:

(i) Shall be repeated at least monthly where any employee is exposed, without regard to the use of respirators, in excess of the permissible exposure limit.

(ii) Shall be repeated not less than quarterly where any employee is exposed, without regard to the use of respirators, in excess of the action level.

(iii) May be discontinued for any employee only when at least two consecutive monitoring determinations, made not less than 5 working days apart, show exposures for that employee at or below the action level.

(3) Whenever there has been a production, process or control change which may result in an increase in the release of vinyl chloride, or the employer has any other reason to suspect that any employee may be exposed in excess of the action level, a determination of employee exposure under paragraph (d) (1) of this section shall be performed.

(4) The method of monitoring and measurement shall have an accuracy (with a confidence level of 95 percent) of

not less than plus or minus 50 percent from 0.25 through 0.5 ppm, plus or minus 35 percent from over 0.5 ppm through 1.0 ppm, and plus or minus 25 percent over 1.0 ppm. (Methods meeting these accuracy requirements are available in the "NIOSH Manual of Analytical Methods").

(5) Employees or their designated representatives shall be afforded reasonable opportunity to observe the monitoring and measuring required by this paragraph.

(e) *Regulated area.* (1) A regulated area shall be established where:

(i) Vinyl chloride or polyvinyl chloride is manufactured, reacted, repackaged, stored, handled or used; and

(ii) Vinyl chloride concentrations are in excess of the permissible exposure limit.

(2) Access to regulated areas shall be limited to authorized persons. A daily roster shall be made of authorized persons who enter.

(f) *Methods of compliance.* Employee exposures to vinyl chloride shall be controlled to at or below the permissible exposure limit provided in paragraph (c) of this section by engineering, work practice, and personal protective controls as follows:

(1) Feasible engineering and work practice controls shall immediately be used to reduce exposures to at or below the permissible exposure limit.

(2) Wherever feasible engineering and work practice controls which can be instituted immediately are not sufficient to reduce exposures to at or below the permissible exposure limit, they shall nonetheless be used to reduce exposures to the lowest practicable level, and shall be supplemented by respiratory protection in accordance with paragraph (g) of this section. A program shall be established and implemented to reduce exposures to at or below the permissible exposure limit, or to the greatest extent feasible, solely by means of engineering and work practice controls, as soon as feasible.

(3) Written plans for such a program shall be developed and furnished upon request for examination and copying to authorized representatives of the Assistant Secretary and the Director. Such plans shall be updated at least every six months.

(g) *Respiratory protection.* Where respiratory protection is required under this section:

(1) The employer shall provide a respirator which meets the requirements of this paragraph and shall assure that the employee uses such respirator, except that until April 1, 1976, wearing of

respirators shall be at the discretion of each employee for exposures not in excess of 25 ppm, measured over any 15-minute period. Until April 1, 1976, each employee who chooses not to wear an appropriate respirator shall be informed at least quarterly of the hazards of vinyl chloride and the purpose, proper

<i>Atmospheric concentration of vinyl chloride</i>	<i>Required apparatus</i>
(i) Unknown, or above 3,600 ppm.....	Open-circuit, self-contained breathing apparatus, pressure demand type, with full facepiece.
(ii) Not over 3,600 ppm.....	(A) Combination type C supplied air respirator, pressure demand type, with full or half facepiece, and auxiliary self-contained air supply; or
(iii) Not over 1,000 ppm.....	(B) Combination type, supplied air respirator continuous flow type, with full or half facepiece, and auxiliary self-contained air supply.
(iv) Not over 100 ppm.....	Type C supplied air respirator, continuous flow type, with full or half facepiece, helmet or hood. (A) Combination type C supplied air respirator demand type, with full facepiece, and auxiliary self-contained air supply; or (B) Open-circuit self-contained breathing apparatus with full facepiece, in demand mode; or (C) Type C supplied air respirator, demand type, with full facepiece.
(v) Not over 25 ppm.....	(A) A powered air-purifying respirator with hood, helmet, full or half facepiece, and a canister which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm, or (B) Gas mask, front- or back-mounted canister which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm.
(vi) Not over 10 ppm.....	(A) Combination type C supplied-air respirator, demand type, with half facepiece, and auxiliary self-contained air supply; or (B) Type C supplied-air respirator, demand type, with half facepiece; or (C) Any chemical cartridge respirator with an organic vapor cartridge which provides a service life of at least 1 hour for concentrations of vinyl chloride up to 10 ppm.

use, and limitations of respiratory devices.

(2) Respirators shall be selected from among those jointly approved by the Mining Enforcement and Safety Administration, Department of the Interior, and the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(3) A respiratory protection program meeting the requirements of § 1910.134 shall be established and maintained.

(4) Selection of respirators for vinyl chloride shall be as follows:

(5) (i) Entry into unknown concentrations or concentrations greater than 36,000 ppm (lower explosive limit) may be made only for purposes of life rescue; and

(ii) Entry into concentrations of less than 36,000 ppm, but greater than 3,600 ppm may be made only for purposes of life rescue, firefighting, or securing equipment so as to prevent a greater hazard from release of vinyl chloride.

(6) Where air-purifying respirators are used:

(i) Air-purifying canisters or cartridges shall be replaced prior to the expiration of their service life or the end of the shift in which they are first used, whichever occurs first, and

(ii) A continuous monitoring and alarm system shall be provided where concentrations of vinyl chloride could reasonably exceed the allowable concentrations for the devices in use. Such system shall be used to alert employees when vinyl chloride concentrations exceed the allowable concentrations for the devices in use.

(7) Apparatus prescribed for higher concentrations may be used for any lower concentration.

(h) *Hazardous operations.* (1) Employees engaged in hazardous operations, including entry of vessels to clean polyvinyl chloride residue from vessel walls, shall be provided and required to wear and use;

(i) Respiratory protection in accordance with paragraphs (c) and (g) of this section; and

(ii) Protective garments to prevent skin contact with liquid vinyl chloride or with polyvinyl chloride residue from vessel walls. The protective garments shall be selected for the operation and its possible exposure conditions.

(2) Protective garments shall be provided clean and dry for each use.

(i) *Emergency situations.* A written operational plan for emergency situations shall be developed for each facility storing, handling, or otherwise using vinyl chloride as a liquid or compressed gas. Appropriate portions of the plan shall be implemented in the event of an emergency. The plan shall specifically provide that:

(1) Employees engaged in hazardous operations or correcting situations of existing hazardous releases shall be equipped as required in paragraph (h) of this section;

(2) Other employees not so equipped shall evacuate the area and not return until conditions are controlled by the methods required in paragraph (f) of this section and the emergency is abated.

(j) *Training.* Each employee engaged in vinyl chloride or polyvinyl chloride operations shall be provided training in a program relating to the hazards of vinyl chloride and precautions for its safe use.

(1) The program shall include:

(i) The nature of the health hazard from chronic exposure to vinyl chloride including specifically the carcinogenic hazard;

(ii) The specific nature of operations which could result in exposure to vinyl chloride in excess of the permissible limit and necessary protective steps;

(iii) The purpose for, proper use, and limitations of respiratory protective devices;

(iv) The fire hazard and acute toxicity of vinyl chloride, and the necessary protective steps;

(v) The purpose for and a description of the monitoring program;

(vi) The purpose for, and a description of, the medical surveillance program;

(vii) Emergency procedures;

(viii) Specific information to aid the employee in recognition of conditions which may result in the release of vinyl chloride; and

(ix) A review of this standard at the employee's first training and indoctrination program, and annually thereafter.

(2) All materials relating to the program shall be provided upon request to the Assistant Secretary and the Director.

(k) *Medical surveillance.* A program of medical surveillance shall be instituted for each employee exposed, without regard to the use of respirators, to vinyl chloride in excess of the action level. The program shall provide each such employee with an opportunity for examinations and tests in accordance with this paragraph. All medical examinations and procedures shall be performed by or under the supervision of a licensed physician, and shall be provided without cost to the employee.

(1) At the time of initial assignment, or upon institution of medical surveillance:

(i) A general physical examination shall be performed, with specific attention to detecting enlargement of liver, spleen or kidneys, or dysfunction in these organs, and for abnormalities in skin, connective tissues and the pulmonary system (See Appendix A).

(ii) A medical history shall be taken, including the following topics:

(A) Alcohol intake;

(B) Past history of hepatitis;

(C) Work history and past exposure to potential hepatotoxic agents, including drugs and chemicals;

(D) Past history of blood transfusions; and

(E) Past history of hospitalizations.

(iii) A serum specimen shall be obtained and determinations made of:

(A) Total bilirubin;

(B) Alkaline phosphatase;

(C) Serum glutamic oxalacetic transaminase (SGOT);

(D) Serum glutamic pyruvic transaminase (SGPT); and

(E) Gamma glutamyl transpeptidase.

(2) Examinations provided in accordance with this paragraph shall be performed at least:

(i) Every 6 months for each employee who has been employed in vinyl chloride or polyvinyl chloride manufacturing for 10 years or longer; and

(ii) Annually for all other employees.

(3) Each employee exposed to an emergency shall be afforded appropriate medical surveillance.

(4) A statement of each employee's suitability for continued exposure to vinyl chloride including use of protective equipment and respirators, shall be obtained from the examining physician promptly after any examination. A copy of the physician's statement shall be provided each employee.

(5) If any employee's health would be materially impaired by continued exposure, such employee shall be withdrawn from possible contact with vinyl chloride.

(6) Laboratory analyses for all biological specimens included in medical examinations shall be performed in laboratories licensed under 42 CFR Part 74.

(7) If the examining physician determines that alternative medical examinations to those required by paragraph (k)(1) of this section will provide at least equal assurance of detecting medical conditions pertinent to the exposure to vinyl chloride, the employer may accept such alternative examinations as meeting the requirements of paragraph (k)(1) of this section, if the employer obtains a statement from the examining physician setting forth the alternative examinations and the rationale for substitution. This statement shall be available upon request for examination and copying to authorized representatives of the Assistant Secretary and the Director.

(l) *Signs and labels.* (1) Entrances to regulated areas shall be posted with legible signs bearing the legend:

**CANCER-SUSPECT AGENT AREA AUTHORIZED PERSONNEL ONLY**

(2) Areas containing hazardous operations or where an emergency currently exists shall be posted with legible signs bearing the legend:

**CANCER-SUSPECT AGENT IN THIS AREA PROTECTIVE EQUIPMENT REQUIRED AUTHORIZED PERSONNEL ONLY**

(3) Containers of polyvinyl chloride resin waste from reactors or other waste contaminated with vinyl chloride shall be legibly labeled:

**CONTAMINATED WITH VINYL CHLORIDE  
CANCER-SUSPECT AGENT**

(4) Containers of polyvinyl chloride shall be legibly labeled:

**POLYVINYL CHLORIDE (OR TRADE NAME)  
Contains  
VINYL CHLORIDE**

**VINYL CHLORIDE IS A CANCER-SUSPECT AGENT**

(5) Containers of vinyl chloride shall be legibly labeled either:

(i)

**VINYL CHLORIDE  
EXTREMELY FLAMMABLE GAS UNDER PRESSURE  
CANCER-SUSPECT AGENT**

or (ii) In accordance with 49 CFR Parts 170-189, with the additional legend:

**CANCER-SUSPECT AGENT**

applied near the label or placard.

(6) No statement shall appear on or near any required sign, label or instruction which contradicts or detracts from the effect of, any required warning, information or instruction.

(m) *Records.* (1) All records maintained in accordance with this section shall include the name and social security number of each employee where relevant.

(2) Records of required monitoring and measuring, medical records, and authorized personnel rosters, shall be made and shall be available upon request for examination and copying to authorized representatives of the Assistant Secretary and the Director.

(i) Monitoring and measuring records shall:

(A) State the date of such monitoring and measuring and the concentrations determined and identify the instruments and methods used;

(B) Include any additional information necessary to determine individual

employee exposures where such exposures are determined by means other than individual monitoring of employees; and

(C) Be maintained for not less than 30 years.

(ii) Authorized personnel rosters shall be maintained for not less than 30 years.

(iii) Medical records shall be maintained for the duration of the employment of each employee plus 20 years, or 30 years, whichever is longer.

(3) In the event that the employer ceases to do business and there is no successor to receive and retain his records for the prescribed period, these records shall be transmitted by registered mail to the Director, and each employee individually notified in writing of this transfer.

(4) Employees or their designated representatives shall be provided access to examine and copy records of required monitoring and measuring.

(5) Former employees shall be provided access to examine and copy required monitoring and measuring records reflecting their own exposures.

(6) Upon written request of any employee, a copy of the medical record of that employee shall be furnished to any physician designated by the employee.

(n) *Reports.* (1) Not later than 1 month after the establishment of a regulated area, the following information shall be reported to the OSHA Area Director. Any changes to such information shall be reported within 15 days.

(i) The address and location of each establishment which has one or more regulated areas; and

(ii) The number of employees in each regulated area during normal operations, including maintenance.

(2) Emergencies, and the facts obtainable at that time, shall be reported within 24 hours to the OSHA Area Director. Upon request of the Area Director, the employer shall submit additional information in writing relevant to the nature and extent of employee exposures and measures taken to prevent future emergencies of similar nature.

(3) Within 10 working days following any monitoring and measuring which discloses that any employee has been exposed, without regard to the use of respirators, in excess of the permissible exposure limit, each such employee shall be notified in writing of the results of the exposure measurement and the steps

being taken to reduce the exposure to within the permissible exposure limit.

(o) *Effective dates.* (1) Until April 1, 1975, the provisions currently set forth in § 1910.93q of this Part shall apply.

(2) Effective April 1, 1975, the provisions set forth in § 1910.93q of this Part shall apply.

#### APPENDIX A—SUPPLEMENTARY MEDICAL INFORMATION

When required tests under paragraph (k)(1) of this section show abnormalities, the tests should be repeated as soon as practicable, preferably within 3 to 4 weeks. If tests remain abnormal, consideration should be given to withdrawal of the employee from contact with vinyl chloride, while a more comprehensive examination is made.

Additional tests which may be useful:

A. For kidney dysfunction: urine examination for albumin, red blood cells, and exfoliative abnormal cells.

B. Pulmonary system: Forced vital capacity, Forced expiratory volume at 1 second, and chest roentgenogram (posterior-anterior, 14 x 17 inches).

C. Additional serum tests: Lactic acid dehydrogenase, lactic acid dehydrogenase isoenzyme, protein determination, and protein electrophoresis.

D. For a more comprehensive examination on repeated abnormal serum tests: Hepatitis B antigen, and liver scanning.

(Secs. 6 and 8, 84 Stat. 1596, 1599 (29 U.S.C. 655, 657); Secretary of Labor's Order No. 12-71, 35 FR 8754) [39 FR 35896, Oct. 4, 1974; 39 FR 41848, Dec. 3, 1974, as amended at 40 FR 13211, Mar. 25, 1975. Redesignated at 40 FR 23073, May 28, 1975]

## XI. APPENDIX II

### SAMPLING AND ANALYTICAL METHOD FOR VINYL CHLORIDE IN AIR

This is NIOSH-accepted (Classification B) analytical method No. P&CAM 178 for determination of vinyl chloride in air, issued September 3, 1974 and revised January 29, 1976 [245]. This method involves adsorption on activated carbon, desorption with carbon disulfide, and gas chromatography. The range for determination of vinyl chloride using this method is 0.008-5.2 mg/cu m (0.003-2.03 ppm) in a 5-liter air sample. The precision (coefficient of variation-CV(T)) is approximately 0.08 at levels of 7 and 71 mg/cu m (2.73 and 27.7 ppm).

#### Principle of the Method

A known volume of air is drawn through two sorbent tubes in series containing activated carbon (made from coconut shells), which adsorbs the vinyl chloride present in the air sample. The collected vinyl chloride is then desorbed with carbon disulfide, and the resulting solutions are analyzed by gas chromatography with a flame-ionization detector. The areas under the resulting peaks are compared with areas obtained from the injection of standards.

#### Range and Sensitivity

(a) The minimum detectable amount of vinyl chloride was found to be 0.2 ng/injection at a 1 x 1 attenuation of a gas chromatograph. This corresponds to an estimated concentration of 0.008 mg/cu m in a 5-liter air sample analyzed by this method. However, the desorption efficiency from activated carbon of amounts of vinyl chloride as small as 40 ng (0.008 µg/liter x 5 liters) has not been determined. Therefore, the detection limit of the overall method may be somewhat higher than 0.008 mg/cu m.

(b) At a sampling flowrate of 50 ml/minute, the total volume to be sampled should not exceed 5 liters. This value is based on data indicating that more than 10 liters of air containing 2.6 µg/liter (1 ppm) of vinyl chloride could be sampled on activated carbon before 5% breakthrough was observed. This would indicate that 5 liters of air containing no more than 5.2 mg/cu m may be sampled without significant breakthrough. If a particular atmosphere is suspected of containing a high concentration of contaminants or a high humidity is suspected, the sampling volume should be reduced by 50%. A safety factor has been included in the 5-liter volume, and the capacity of the first tube should be adequate within these limits except under the most extreme conditions.

### Interferences

(a) When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped effectively. Experiments indicate that high humidity severely decreases the capacity of activated carbon for organic vapors.

(b) When two or more substances are known or suspected to be present in the air, this information, including their suspected identities, should be transmitted with the sample, since these compounds may interfere with the analysis for vinyl chloride.

(c) Any compound that has the same retention time as vinyl chloride under the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, may not provide proof of chemical identity. Often, operating conditions can be modified to eliminate interferences. Samples should be analyzed by an independent method when overlapping gas-chromatographic peaks cannot be resolved.

### Precision and Accuracy

(a) A coefficient of variation of 0.076 was obtained from analysis of each of two sets of sorbent tubes, one set of 27 tubes exposed to vinyl chloride at a concentration of 7.2 mg/cu m in air and another set of 29 tubes exposed at a concentration of 71.3 mg/cu m. These values reflect total sampling and analytical error as well as desorption efficiency correction errors.

(b) Experiments were performed to obtain some indication of the accuracy of this method, although accuracy was difficult to evaluate. These experiments generally involved six sorbent tube samples exposed to a synthetic atmosphere. The calculated value was the concentration expected based on the measured amounts of vinyl chloride and air mixed to prepare the synthetic atmosphere. The calculated value was not the true value, since it was subject to experimental error. The value found from analysis of each sorbent tube, after correction for desorption efficiency, was also compared with that found by the direct injection of gas samples from the same synthetic atmosphere used in loading the tubes. The results of these experiments are shown in Table XI-1. It should be noted that average concentrations determined by analysis of sorbent tubes were within 6% of the average concentrations determined by analysis of gas samples.

TABLE XI-1

## ACCURACY OF THE RECOMMENDED SAMPLING METHOD FOR VINYL CHLORIDE

Experiment Number	Samples	Calculated Concentration (mg/cu m)	Experimental Concentration* (mg/cu m)	Estimated Error** (%)
I	Gas samples	64	71.2 ±0.7	-2
	Solvent tubes	64	69.8 ±1.5	
II	"	13	14.5 ±0.5	-6
		13	13.6 ±0.4	
III	"	2.6	2.88 ±0.07	+1
		2.6	2.91 ±0.13	
IV	"	1.3	-	-
		1.3	1.27 ±0.09	

\*Average of concentrations determined from sorrent tubes minus average of concentrations determined from gas samples, divided by average of concentrations determined from gas samples, x 100

\*\*Mean value ±95% confidence level (standard deviation x Student's t at 0.05 significance level, divided by square root of number of samples)

#### Advantages and Disadvantages of the Method

(a) The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by a rapid instrumental method. The method can also be used for the simultaneous determination of two or more components suspected to be present in the same sample by changing gas-chromatographic conditions from isothermal to a temperature-programmed mode of operation.

(b) One disadvantage of the method is that the amount of sample that can be taken is limited by the amount of vinyl chloride that the tube will hold before it becomes overloaded. When the value obtained for the backup section of the sorbent tube exceeds 20% of that found on the front section, there is a possibility of sample loss. During storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time, 33% of these compounds will be found in the backup section. This

may lead to some confusion as to whether sample loss has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20 C or by using two separately capped tubes for the front and backup sections.

(c) The precision of the method is limited by the reproducibility of the pressure drop and, therefore, by the flowrates across the tubes. Because the pump is usually calibrated for one particular tube, differences in flowrates from tube to tube can cause sample volumes to vary.

#### Apparatus

(a) Personal sampling pump: The pump should be a properly calibrated personal sampling pump for personal and area samples. The pump should also be capable of accurate performance at the recommended flowrates. It should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or a glass rotameter that will determine the flowrate to within  $\pm 5\%$  may be used for the calibration.

(b) Sorbent tubes: The glass tubes are flame sealed at both ends. Each is 7 cm long, 6-mm outer diameter, 4-mm inner diameter, and contains two sections of 20/40-mesh activated carbon separated by a 3-mm portion of urethane foam. The activated carbon is prepared from coconut shells and is fired at 600 C prior to packing to remove adsorbed materials. The primary adsorbing section contains 100 mg of sorbent, the backup section 50 mg. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2 inches of water at a flowrate of 0.2 liters/minute.

(c) Gas chromatograph equipped with a flame-ionization detector.

(d) Stainless steel column (20 feet x 0.125 inch) packed with 10% SE-30 on 80/100 mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). Other columns capable of performing the required separations may be used.

(e) A mechanical or electronic integrator and a recorder or some method for determining peak area.

(f) Vials (2 ml) that can be sealed with caps containing Teflon-lined silicone rubber septa.

(g) Microliter syringes (10  $\mu$ l and other convenient sizes for making standards).

(h) Gastight syringe (1 ml, with a gastight valve).

(i) Pipets (0.5-ml delivery pipets or 1.0-ml pipets graduated in 0.1-ml increments).

(j) Volumetric flasks (10 ml or convenient sizes for making solutions), preferably with plastic stoppers.

(k) Gas bags, Tedlar or equivalent.

#### Reagents

- (a) Carbon disulfide, "spectroquality" or better grade.
- (b) Vinyl chloride, lecture bottle, 99.9% minimum purity.
- (c) Toluene, chromatographic quality.
- (d) Helium, Bureau of Mines grade A.
- (e) Frepurified hydrogen.
- (f) Filtered, compressed air.

#### Procedure

##### (a) Collection and Shipping of Samples

(1) Immediately before sampling, break the ends of the two tubes to provide an opening of at least 2 mm, one-half the internal diameter of the tube.

(2) Position the second sorbent tube next to the sampling pump in tandem with the first tube, to serve as a backup. If one tube is used, position the smaller section of tube nearest the sampling pump.

(3) Place the sorbent tubes in a vertical position with the larger section of sorbent pointing up during sampling to minimize channeling of the vinyl chloride through the sorbent.

(4) Do not allow air being sampled to pass through any hose or tubing before entering the sorbent tubes.

(5) Measure the flowrate and time, or the sampling volume, as accurately as possible. Take the sample at a flowrate of 50 ml/minute. The maximum volume to be sampled should not exceed 5 liters.

(6) Sample relatively large volumes (10-20 liters) of air through other sorbent tubes at the same time personal samples are taken. These bulk air samples will be used by the analyst to identify possible interferences before the personal samples are analyzed.

(7) Measure and record the temperature and pressure of the atmosphere being sampled if they are significantly different from 25 C or 760 mmHg.

(8) Cap the sorbent tubes with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

(9) Treat one tube in the same manner as a sample tube (break, seal, and transport), but do not sample any air through the tube. This tube is labeled as a blank.

(10) Pack capped tubes tightly to minimize tube breakage during transport to the laboratory. The use of two tubes in series during sampling eliminates the need for cooling during shipping. However, if only one tube is used, and if the samples will spend a day or more in transit, then cool the tubes, eg, with dry ice, to minimize migration of the vinyl chloride to the backup section.

(11) Samples received at the laboratory are logged in and immediately stored in a freezer (around -20 C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20 C, vinyl chloride will equilibrate between the two sections of activated carbon in one tube, ie, it will migrate to the backup section. This phenomenon is observable after 2 weeks and may be confused with sample loss after 1-2 months.

(b) Analysis of Samples

(1) Cleaning of Equipment. All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with tapwater and distilled water.

(2) Preparation and Desorption of Samples. The two tubes used in the collection of a single sample are analyzed separately. If only one tube is used for sampling, then each section of activated carbon should be analyzed separately. Discard the glass wool from each tube. Transfer both sections of each tube to a small vial containing 1 ml of the precooled carbon disulfide. It is important to add the sorbent to carbon disulfide and not the carbon disulfide to the sorbent. Top vial with a septum cap. Discard the separating section in each tube. Tests indicate that desorption is complete in 30 minutes if the sample is agitated occasionally during this period. The samples should be analyzed within 60 minutes after addition to carbon disulfide.

(3) Gas-Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

- (A) Helium carrier gas flow, 40 ml/minute (80 psig).
- (B) Hydrogen gas flow to detector, 65 ml/minute (20 psig).
- (C) Airflow to detector, 500 ml/minute (50 psig).
- (D) Injector temperature, 230 C.
- (E) Detector temperature, 230 C.
- (F) Column temperature, 60 C.

(4) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, use the solvent flush injection technique. Flush a 10- $\mu$ l syringe with solvent several times to wet the barrel and plunger. Draw 2  $\mu$ l of solvent into the syringe to increase the accuracy and reproducibility of the injected sample volume. Remove the needle from the solvent and pull the plunger back about 0.4  $\mu$ l to separate the solvent flush from the sample with a pocket of air to be used as a marker. Then immerse the needle in the sample and withdraw a 5- $\mu$ l aliquot to the 7.4- $\mu$ l mark (2  $\mu$ l of solvent + 0.4  $\mu$ l of air + 5  $\mu$ l of sample = 7.4  $\mu$ l). After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Make duplicate injections of each sample and standard. No more than a 3% difference in area from repeated injections is to be expected. Automatic sampling devices may also be used. A syringe equipped with a Chaney adapter may also be used in lieu of the solvent flush technique.

(5) Measurement of Area: Measure the area under the sample peak using an electronic integrator or some other suitable form of area measurement. Area measurements are compared with a standard curve prepared as discussed in Preparation of Standards. Preliminary results are read from a standard curve prepared as discussed below.

(c) Determination of Desorption Efficiency

(1) Importance of Determination. The efficiency of desorption of a particular compound can vary from one laboratory to another and also from one batch of sorbent to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the desorption process. Desorption efficiency should be determined on the same batch of sorbent tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube), particularly at lower values, eg, 2.5  $\mu$ g.

(2) Procedure for Determining Desorption Efficiency. Sorbent tubes from the same batch as that used in obtaining samples are used in this determination. Inject a measured volume of vinyl chloride gas into a bag containing a measured volume of air. The concentration in the bag may be calculated if room temperature and pressure are known. The bag is made of Tedlar (or other material that will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. Sample a measured volume from the bag through a sorbent tube using a calibrated sampling pump. Prepare at least five tubes in this manner. These tubes are desorbed and analyzed in the same manner as the samples. Samples taken with a gastight syringe from the bag are also injected into the gas chromatograph. The concentration in the bag (standard) is compared with the concentration obtained from the tube (sample).

The desorption efficiency equals the amount of vinyl chloride desorbed from the charcoal divided by the product of the vinyl chloride concentration in the bag times the volume of synthetic atmosphere sampled, or:

$$\frac{\text{(amount of vinyl chloride desorbed from sorbent)}}{\text{(vinyl chloride concentration in bag) x (volume of atmosphere sampled)}}$$

#### Preparations of Standards

Caution: These laboratory operations involve carcinogens.

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this compound.

A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas-chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in  $\mu\text{g}/\text{ml}$  vs peak area or peak height. There are two methods of preparing standards, and they are comparable if highly purified vinyl chloride is used. If no internal standard is used in the method, standard solutions must be analyzed at the same time as the sample. This will minimize the effect of day-to-day variations of the flame-ionization response.

(a) Gravimetric Method. Slowly bubble vinyl chloride into a weighed 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, weigh the flask again. A weight change of 100-300 mg will usually be observed. Dilute the solution to exactly 10 ml with carbon disulfide and use to prepare other standards by removing aliquots with syringes of various sizes. Subsequent dilution of these aliquots with carbon disulfide results in a series of standards that have linear values from the range of 0.2  $\mu\text{g}/\text{injection}$ , the minimum detectable amount of vinyl chloride, to 1.5  $\mu\text{g}/\text{injection}$ .

(b) Volumetric Method. Draw a 1-ml gas sample of pure vinyl chloride into a gastight syringe and close the syringe valve. Insert the tip of the needle into a 10-ml volumetric flask containing approximately 5 ml of carbon disulfide. Open the syringe valve and withdraw the plunger slightly to allow the carbon disulfide to enter the syringe. Return the solution in the syringe to the flask and rinse the syringe with clean carbon disulfide, adding the washings to the volumetric flask. Fill the volumetric flask to the mark with carbon disulfide. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20 C and have been found to be stable at this temperature for 3 days. Tight-fitting plastic tops on the volumetric flasks seem to retain the vinyl chloride better than ground-glass stoppers.

### Calculations

(a) The weight, in  $\mu\text{g}$ , corresponding to the area under each peak is read from the standard curve for vinyl chloride. No liquid volume corrections are needed because both the standards and the samples are based on the number of  $\mu\text{g}$  in 1.0 ml of carbon disulfide and the volume injected in both cases is identical.

(b) Corrections for the blank are made for each sample:

$$\mu\text{g} = \mu\text{g}(\text{sample}) - \mu\text{g}(\text{blank})$$

A similar procedure is followed for the backup sections.

(c) Add the amounts present in the front and backup sections of the same sample tube to determine the total amount of vinyl chloride in the sample.

(d) The total amount is corrected for the desorption efficiency at the level of vinyl chloride measured:

$$\text{Corrected amount (in } \mu\text{g)} = \frac{\text{amount (in } \mu\text{g)}}{\text{desorption efficiency}}$$

(e) The concentration of vinyl chloride in air may be expressed in mg/cu m:

$$\text{mg/cu m} = \frac{\text{corrected weight (in } \mu\text{g)}}{\text{volume of air sampled (in liters)}}$$

(f) The concentration may also be expressed in terms of ppm by volume:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{T+273}{293}$$

where:

24.45 = molar volume (liters/mole) at 25 C and 760 mmHg

MW = molecular weight

P = pressure (mmHg) of air sampled

T = temperature (C) of air sampled

## XII. APPENDIX III

### SAMPLING AND ANALYTICAL METHOD FOR VINYLIDENE CHLORIDE IN AIR

This is the NIOSH-proposed (Classification E) analytical method No. P&CAM 266 for determination of vinylidene chloride in air issued November 21, 1977 [259]. This method involves adsorption on charcoal, desorption with carbon disulfide, and gas chromatography. The range for determination of vinylidene chloride using this method is 2-12 mg/cu m (0.5-3.02 ppm) in 7 liters of air. The precision (pooled relative standard deviation) is approximately 5% for analysis of samples containing 12-85  $\mu\text{g}$  of vinylidene chloride/sample.

#### Synopsis

(a) A known volume of air is drawn through a charcoal tube to trap the vinylidene chloride present.

(b) The charcoal in the tube is transferred to a small vial where the vinylidene chloride is desorbed with carbon disulfide.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

(d) The area or the height of the resulting peak is determined and compared with either the peak areas or heights obtained from injection of standards.

#### Working Range, Sensitivity, and Detection Limit

(a) The method was tested with sample loading between 12 and 85  $\mu\text{g}$  of vinylidene chloride/charcoal tube. The samples were collected from atmospheres containing vinylidene chloride in the range of 7.6-10.0 mg/cu m and having a relative humidity of greater than 80%.

(b) The slope of the calibration curve (response vs weight/sample) was 0.0322 area count/ $\mu\text{g}$  when analysis was done by electronic integration. When analysis was done using peak height, the slope of the calibration curve was  $4.75 \times 10^{-12}$  amps/ $\mu\text{g}$ .

(c) The lowest quantifiable limit for this method was determined to be 7  $\mu\text{g}$  of vinylidene chloride/sample. At this level the relative standard deviation of replicate samples was found to be less than 10% and the

desorption efficiency was greater than 80%. This limit could be lower if the charcoal used is shown to give better desorption characteristics at the lower level.

### Interferences

(a) When two or more substances are known or suspected to be present in the air, this information, including their suspected identities, should be transmitted with the sample, since these compounds may interfere with the analysis for vinylidene chloride.

(b) Any compound that has the same retention time as vinylidene chloride under the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

(c) If the possibility of interference exists, separation conditions, eg, column packing, temperature, carrier flow, and detector, must be changed to circumvent the problem.

### Precision and Accuracy

(a) The pooled relative standard deviation of the analytical method was 4.8% for the analysis of 36 samples over the range of 12-85  $\mu\text{g}$  vinylidene chloride/sample.

(b) The concentration of the sampled air was also determined using a gas phase infrared analyzer. The gas-chromatographic determinations averaged 5% lower when compared with the results of the infrared analyzer. No desorption efficiency corrections were used.

(c) The breakthrough volume and, therefore, the capacity of charcoal for vinylidene chloride decreased with increasing relative humidity. At 87% relative humidity the breakthrough volume was 10% of the breakthrough volume at 10% relative humidity. The breakthrough volume was also found to be a function of concentration of vinylidene chloride. When high relative humidity air containing 144 mg/cu m of vinylidene chloride was sampled at 0.2 liter/minute the breakthrough volume was 3.7 liters. At a vinylidene chloride concentration of 10 mg/cu m and high relative humidity the breakthrough volume was 7.3 liters.

(d) Samples of vinylidene chloride on charcoal were found to be stable at 25 C for 7 days and for 21 days if stored at 5 C for the remainder of the period.

### Advantages and Disadvantages of the Method

(a) The sampling device is small, portable, and involves no liquids. Many of the interferences can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method.

(b) One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the charcoal tube. When the sample value obtained for the backup section of the charcoal tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage the volatile compounds may migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section). This can be minimized by storing the samples in a refrigerator until the analysis is performed.

(c) The precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variation in pressure drop will affect the flowrate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

(d) The recommended gas-chromatographic packing will not separate vinyl chloride and carbon disulfide. Other gas-chromatographic packings that separate vinyl chloride and carbon disulfide do not separate vinylidene chloride and carbon disulfide. If analysis for each of these monomers is to be performed, it is necessary to use different columns to analyze the samples.

### Apparatus

(a) Personal sampling pump capable of accurate performance at 0.2 liter/minute and calibrated with a representative charcoal tube in the line.

(b) Charcoal tubes: Glass tubes with both ends flame-sealed, 7 cm long with a 6-mm outer diameter, and a 4-mm inner diameter, containing two sections of 20/40-mesh activated carbon separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 0.2 liter/minute.

(c) Gas chromatograph equipped with a flame-ionization detector. Optional: electronic integrator.

(d) Silanized glass gas-chromatographic column (10 feet x 1/4-inch outer diameter) packed with Durapak OPN 100/120 mesh. Any gas-chromatographic column capable of separating carbon disulfide and vinylidene chloride may be used.

(e) Vials (2 ml) that can be sealed with caps containing Teflon-lined silicone rubber septa.

(f) Microliter syringes, 10  $\mu$ l, and convenient sizes for making standards.

(g) Pipet, 1.0 ml.

### Reagents

All reagents used should be ACS Reagent Grade or better.

(a) Carbon disulfide, "spectroquality" or better.

(b) Vinylidene chloride, 99%.

(c) Cyclohexane.

(d) Helium, Bureau of Mines grade A.

(e) Prepurified hydrogen.

(f) Filtered, compressed air.

### Procedure

(a) Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be washed with detergent and rinsed thoroughly with tap water and distilled water.

(b) Collection and Shipping of Samples

(1) Immediately before sampling, the ends of the tube are broken to provide an opening (2 mm) at least one-half the internal diameter of the tube.

(2) The tube is connected to the sampling pump via rubber tubing. The smaller section of charcoal is the backup and is positioned nearest the sampling pump.

(3) The charcoal tube should be vertical during sampling to prevent channeling through the tube.

(4) Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

(5) Measure and report the flowrate and time, or the sampling volume, as accurately as possible. The sample is taken at 0.2 liter/minute or less. The maximum volume sampled should not exceed 7.0 liters.

(6) Measure and record the temperature and pressure of the atmosphere being sampled.

(7) Cap the charcoal tubes with the plastic caps supplied immediately after sampling. Under no circumstances should rubber caps be used.

(8) For every 10 samples taken, one charcoal tube should be handled in the same manner as the samples (break, seal, and transport), except that no air is sampled through this tube. This should be labeled as a blank.

(9) If samples are shipped to a laboratory, they should be packed tightly to minimize tube breakage during shipping.

(10) Six to twelve unopened charcoal tubes should also be shipped so desorption efficiency studies can be performed on the same type and lot of charcoal used for sampling.

(11) Samples received at the laboratory are logged in and immediately stored in a refrigerator.

(c) Analysis of Samples

(1) Preparation of Samples. The charcoal tubes are removed from the refrigerator and permitted to equilibrate to room temperature to prevent water condensation on the cold charcoal. Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The front section (larger) is transferred to a small vial. The separating foam is removed from the tube and discarded. The backup section is also transferred to a small vial. The contents of each individual tube are desorbed before the next sample tube is opened.

(2) Desorption of Samples. After the two sections of a charcoal tube are transferred to small vials, 1.00 ml of carbon disulfide is pipetted into each of the two vials. A serum cap is then crimped into place immediately after the carbon disulfide has been added. (All work with carbon disulfide should be performed in a hood because of the high toxicity of carbon disulfide). The capped samples are kept at room temperature with occasional agitation. Desorption is complete in 30 minutes. The samples should be analyzed the same day they are desorbed.

(3) Gas-Chromatographic Conditions:

(A) 70 ml/minute helium carrier flow.

- (B) 50 ml/minute hydrogen flow to detector.
- (C) 500 ml/minute air flow to detector.
- (D) 150 C injector temperature.
- (E) 200 C manifold (detector) temperature.
- (F) 65 C (isothermal) oven temperature.

Under these conditions the capacity ratio for vinylidene chloride was 5.2.

(4) Injection. Inject a 5- $\mu$ l aliquot into the gas chromatograph. A syringe equipped with a Chaney adapter may be used in lieu of the solvent flush technique.

(5) Measurement of Area: Measure the area under the sample peak using an electronic integrator or another suitable form of area measurement. Area measurements are compared with a standard curve prepared as discussed in Preparation of Standards.

(6) Measurement of Peak Height. The product of peak height and attenuator setting is linear over the analytical range. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Preliminary results are read from a standard curve prepared as discussed below.

(d) Determination of Desorption Efficiency

(1) Importance of Determination. The desorption efficiency of a particular compound can vary between laboratories and batches of charcoal. Also, for a given batch of charcoal the desorption efficiency can vary with the weight of contaminant adsorbed. The charcoal used for the study of this method gave a desorption efficiency of 80% for a loading of 7  $\mu$ g of vinylidene chloride/100 mg bed of charcoal.

(2) Procedure for Determining Desorption Efficiency. The desorption efficiency should be determined at three levels with a minimum of three samples at each level. Vinylidene chloride can be dissolved in cyclohexane to give stock solutions. The concentrations should be such that no more than 8  $\mu$ l of a stock solution will be injected onto the charcoal. Activated charcoal in an amount equivalent to that found in the larger section of the charcoal tube (100 mg) is placed in a small vial and capped. An aliquot of the stock solution is injected into the charcoal tube. Two of the levels should reflect the extremes of the analytical range while the third level is inbetween the high and low levels. Each vial is allowed to stand overnight to assure complete adsorption of vinylidene chloride onto the charcoal. Standards are

prepared by injecting an identical amount of cyclohexane stock solution into 1.0 ml of carbon disulfide. The samples and standards are analyzed as described in Analysis of Samples.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary. The desorption efficiency curve is constructed by plotting the amount of vinylidene chloride found in a sample vs the desorption efficiency.

#### Calibration and Standardization

CAUTION: Vinylidene chloride has been tentatively identified as a carcinogen. Precautions must be taken while handling this compound to prevent contamination of personnel and the working area.

It is convenient to express the concentration of standards in terms of  $\mu\text{g}/1.0$  ml of carbon disulfide or  $\mu\text{g}/\text{sample}$ . The density of vinylidene chloride is used to convert the volume taken to the mass taken ( $1.218 \text{ mg}/\mu\text{l}$ ). A series of standards varying in concentration over the range of interest is prepared and analyzed under the same gas-chromatographic conditions and during the same time period as the samples. It is best to alternate standard then sample, during the analysis. Curves are established by plotting the concentration of the standards in  $\mu\text{g}/1.0$  ml of carbon disulfide vs peak area or peak height.

#### Calculations

(a) The sample weight in  $\mu\text{g}$  is read from the standard curve.

(b) Blank corrections are not expected but, if the analysis shows a blank correction is needed, the correction is:

$$WF = Ws - Wb$$

where:

WF = corrected amount ( $\mu\text{g}$ ) on the front section of the charcoal tube

Ws = amount found on the front section of the charcoal tube

Wb = amount ( $\mu\text{g}$ ) found on the front section of the blank charcoal tube

A similar procedure is followed for the backup sections.

(c) A correction for desorption efficiency is made:

$$MF = \frac{WF}{D}$$

where:

MF = corrected amount ( $\mu\text{g}$ )  
WF = amount ( $\mu\text{g}$ ) after blank correction  
D = desorption efficiency corresponding to  
the weight WF

The corrected amount of the backup section, MB, is similarly calculated.

(d) The concentration, C, of vinylidene chloride in the air sampled is expressed in mg/cu m, which is numerically equal to  $\mu\text{g/liter}$ :

$$C = \frac{MF + MB}{V}$$

where:

MF = amount of vinylidene chloride found on front  
section in  $\mu\text{g}$   
MB = amount of vinylidene chloride found on backup  
section in  $\mu\text{g}$   
V = volume of air sampled in liters

(e) If desired the results may be expressed in ppm at 25 C (298 K) and 760 mmHg:

$$C(\text{ppm}) = C(\mu\text{g/liter}) \times \frac{24.45}{96.6} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure of air sampled in mmHg  
T = temperature of air sampled in C  
24.45 = molar volume at 25 C and 760 mmHg in liters/mol  
96.9 = molecular weight of vinylidene chloride in g/mol